Oxytetracycline Degradation by Heat-Activated Peroxydisulfate and Peroxymonosulfate Oxidation: Optimization by Box-Behnken Design

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**Oxytetracycline Degradation by Heat-Activated Peroxydisulfate and Peroxymonosulfate
Oxidation: Optimization by Box-Behnken Design**

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ABSTRACT

This study investigates the removal of oxytetracycline performed by persulfate (PS) and peroxymonosulfate (PMS) processes. For this purpose, response surface methodology was used to examine the effectiveness of PS and PMS processes under both alkaline and thermal conditions. The effect of four independent variables, which were selected as pH, PS/PMS concentration, temperature, and time, were analyzed in a wide range. The working pH was between pH 3–11 to compare acidic and alkaline conditions, and the temperature was selected between 30 and 90 °C to evaluate the effect of thermal activation of sulfate radicals for both processes. According to the results of prepared Response Surface Methodology (RSM) models, all four independent variables were determined to be highly significant for both PS and PMS. Especially in the PMS process, the highest PMS concentration was observed to complete degradation of OTC. The conditions for the highest removal were pH 9 and PS/PMS concentration was approximately 4mM for both processes, while the temperature and required time were 72.9°C and 75°C, 26.5 min and 20 min, for PS and PMS processes, respectively. PS process has higher kinetic constants at all pH values than the PMS process.

Keyword: Antibiotic, Persulfate Activation, Peroxymonosulfate Activation, Sulfate radicals, Hydroxyl radicals

1 Introduction

With industrialization, environmental pollution has become an important problem for all living beings; especially these effects are observed at the points where the chemicals used end up with

the discharge or release. One of these emerging chemicals is broad-spectrum antibiotics, which are used to treat infections in humans and animals. Oxytetracycline (OTC) is a low-cost prophylactic antibiotic with broad-spectrum activity, one of the tetracycline (TC) group antibiotics. Although it is for humanitarian purposes, it is a pharmaceutical pollutant that is frequently used as a supplement in the breeding of livestock (Lai et al., 2020). It is a recalcitrant pharmaceutical pollutant for biodegradation, showing that it will be abundant in the aquatic environment for many years. OTC, which has been started to be investigated due to its encounter in aquatic environments (lakes, rivers, etc.), remains in nature for a long time due to its persistence and poses a threat to the deterioration of the ecosystem by triggering the formation of antibiotic-resistant bacteria. Therefore, OTC was chosen as the target pollutants to be degraded by persulfate and peroxymonosulfate processes.

Due to the ineffectiveness of traditional biological treatment methods, especially advanced oxidation techniques are among the issues that need to be investigated (Cuerda-Correa et al., 2020). Today, many advanced oxidation processes are successfully applied in many treatment facilities (Ulucan-Altuntas and Ilhan, 2018; Basturk et al., 2020; Can-Guven et al., 2020). From this viewpoint, the Fenton process is used as the most common oxidation process (Zhang et al., 2017; Han et al., 2020; Lai et al., 2020), and several authors have reported that ozone (Li et al., 2008), UV (Yan et al., 2020), photocatalytic membrane reactors (Espíndola et al., 2019) are also effective for OTC degradation. Among the studies conducted for the last decade, advanced oxidation processes (AOPs) based on persulfate activation (PS) are one of the promising methods for the treatment of recalcitrant pollutants. When it reacts with hydroxyl radicals, sulfate radicals with a high oxidative ability and longer life than other active species are formed. Persulfate (PS) and peroxymonosulfate (PMS) are the most effective oxidants in the production of sulfate radicals (Li et al., 2020). So far, the use of ultraviolet (Ao et al., 2019; Bi et al., 2020), microwave (Genc et al., 2020), sonication (Cherifi et al., 2019), heat treatment (Can-Guven et al., 2020), and transition metal ions (Malakotian et al., 2019; Bi et al., 2020) in PS and PMS activation has been tried in the removal of recalcitrant contaminants. Compared to the Fenton process, it has the potential to replace Fenton process applications since it is easier to store and transport persulfate than H_2O_2 .

While heat is effective in activating PS and PMS, it can also improve the degradation of the organic compound. The heat activation of PS and PMS occurs by breaking the single bond between the

oxygenes. The equation showing the formation of sulfate radicals by activation of PS and PMS is as follows (Eq.1 and Eq.2):

As can be understood from Eq1 and Eq.2, only sulfate radicals are formed in PS activation, while by using PMS, sulfate radical ($SO_4 \cdot$) and hydroxyl radicals ($\cdot OH$) can be formed. However, the reaction of water and $SO_4 \cdot$ radicals to form $\cdot OH$ radicals is too slow to be significant in most processes, it is stated in the literature that $SO_4 \cdot$ radicals transform more quickly into $\cdot OH$ radicals with the effect of temperature and pH (Eq.3).

It has been encountered in some studies that $SO_4 \cdot$ radicals are effective when pH is acidic, and hydroxyl radicals are seen in PS activation when pH is alkaline. Besides, PS can be activated only by adjusting the pH to alkaline conditions. In this mechanism, the perhydroxyl radicals formed to play an active role in the formation of sulfate radicals (Eq.4 and Eq.5), hydroxyl radicals (Eq. 6), and superoxides (Eq. 5) (Wang and Wang, 2018).

Although there are studies conducted with heat and alkaline environment activation of PS, the number of studies with PMS is quite limited. According to the studies, it is also seen that the effect of the inlet pH changes on the degradation of different pollutants. Some persulfate and peroxymonosulfate processes made in OTC degradation in the literature are shown in Table 1. It is seen in the studies that UV, transition metal activators, and heat treatment are used as activators. Most of the studies have been done with persulfate activation and it is seen that no comparison with peroxymonosulfate has been made. In the persulfate study activated by heat treatment, it was seen that 2h time was required for complete mineralization.

Table 1. Comparison table of previously published studies

Activator	Treatment Conditions	Degradation Eff.	Ref
UV and pre-magnetized Fe ⁰	OTC Conc. 0.8 mg/L UV Power 6W/L Fe ⁰ 0.1mM, PS 0.1 mM, pH 7.3	approx. 99% in 30 min	(Pan et al., 2019)
Copper Sulphate and UV (solar simulation)	OTC 0.04 mM OTC: Cu ²⁺ :PS=1:1.5:1.75	93.5% in 60 min	(Bi et al., 2020)
Thermo activated	OTC 0.03 mM PS: 2mM Temperature 50°C pH:7	100% in 240 min	(Ji et al., 2016)
UV/PS/Cu/NaHCO ₃	OTC: 0.01 mM, PS: 1 mM Cu : 0.01 mM NaHCO ₃ : 6 mM UV 80 mJ/cm ²	approx. 99%	(Liu et al., 2016a)
Biochar and Bentonite supported Fe ⁰	OTC 10 mg/L PMS:0.1mM Biochar supported Fe ⁰ : 0.5 g/L	93% in 5 min	(Li et al., 2020)
Ultrasound/Fe ₃ O ₄	Fe ₃ O ₄ : 0.3 g/L PS: 4 mM TC: 10 mg/L pH10	92.99% in 90 minute	(Malakotian et al., 2019)
Co ₃ O ₄ CNT	OTC: 20 mg/L Catalyst: 1.0g/L	93.6% in 80 min	(Liu et al., 2020)
UV	TTC: 0.045 mM, PMS: 0.2 mM, pH 3.1, UV dose 150 mJ/cm ²	98%	(Ao et al., 2019)

98 Response surface methodology (RSM) is a set of statistical methods used to find the optimum
 99 point based on independent variables. RSM is an experimental design that is widely used, and it
 100 both minimizes the amount of waste that can be generated and provides an optimized result faster.
 101 In light of this information, the effects of PS and PMS on oxytetracycline degradation, activated
 102 by the use of both heat and initial pH, were compared in this study. PS and PMS processes were
 103 evaluated with a 4-factor 5-level central composite design, in which PS/PMS concentration, pH,
 104 temperature, and time were considered as independent variables. According to the optimized
 105 results, the intermediate products were evaluated via UV-vis spectrum. This study is the first study
 106 that compares the PS and PMS processes for OTC degradation.

107 2 Materials and Method

108 2.1 Chemicals and Reagents

109 The chemicals used in this study are in lab quality. Oxytetracycline ($C_{22}H_{24}N_2O_9$) was purchased
110 from Sigma Aldrich (Turkey). Sulfuric acid (H_2SO_4 , purity 98%) and sodium hydroxide (NaOH,
111 purity $\geq 97.0\%$) were obtained from Merck, Turkey, and both were applied in 0.1N and 0.1N
112 concentration for pH adjustment.

113 2.2 Experimental studies and reactor design

114 The experiments were conducted in 50 mL Erlenmeyer flasks placed on a magnetic stirrer with a
115 heater (Weightech Instruments, WH-H320, Turkey). The flasks were closed and the temperature
116 of the samples was measured regularly by a temperature probe during experiments. The pH of each
117 sample was measured before and after the experiments by WTW Multi 9620 IDS, Turkey. The
118 initial concentration of OTC was 10 mg/L and measured at 355 nm wavelength by UV–visible
119 spectrophotometer (WTW–Photolab 6600 UV-vis, Turkey).

120 2.3 Response Surface Methodology

121 Response surface methodology was used to optimize the study both with PS and PMS experiments.
122 Four factor-five level design was applied by performing the independent variables, initial pH (A),
123 PS/PMS concentration (B), initial temperature (C), and time (D) on OTC degradation (y). The
124 levels were coded according to the α value of ± 2 which can be calculated via Eq.7. Actual and
125 coded values of independent variables can be seen in Table 2.

$$\alpha = \frac{x_i - x_o}{\Delta x} \quad (\text{Eq.7})$$

126 In Eq.7, α is code for independent variables, x_i is the actual value of x_i variable, x_o is the actual
127 value in the med-point, and Δx shows the changes in x_i variable. Experimental data were analyzed
128 with the quadratic equation as given in Eq. 8.

$$y = a_0 + \sum a_i x_i + \sum a_{ij} x_i x_j + \sum a_{ii} x_i^2 \quad (\text{Eq.8})$$

In Eq.8, y shows the response value of design, a_0 shows the constant value of design, a_i , a_{ii} and a_{ij} show the coefficients of the linear, quadratic, and interaction, x_i and x_j shows the independent variables. In this study, the response is selected as OTC degradation efficiency. According to selected levels and the number of independent variables, the number of runs in the central composite design (CCD) were given in Table 3.

Table 2. Actual and coded values of independent variables

Variables	Units	Code	Levels				
			-2	-1	0	+1	+2
pH		A	3	5	7	9	11
PS/PMS Concentration	mM	B	1	2	3	4	5
Temperature	°C	C	30	45	60	75	90
Time	min	D	10	20	30	40	50

The OTC degradation efficiencies were calculated according to Eq. (9)

$$\% \text{ OTC Degradation} = \frac{C_0 - C_t}{C_0} \cdot 100 \quad (9)$$

where C_0 and C_t are the initial and effluent OTC concentrations after a treatment time of t , respectively.

Run	pH	PS/PMS Conc.	Temp.	Time	OTC Degradation Efficiency			
					PS Process		PMS Process	
					Y ₁ Actual, %	Y ₁ Predicted, %	Y ₂ Actual, %	Y ₂ Predicted, %
1	5 (-1)	2 (-1)	45 (-1)	20 (-1)	57.60	52.00	46.60	41.83
2	9 (+1)	2 (-1)	45(-1)	20 (-1)	65.50	64.50	56.80	55.12
3	5 (-1)	4 (+1)	45 (-1)	20 (-1)	69.60	68.40	66.76	62.41
4	9 (+1)	4 (+1)	45(-1)	20 (-1)	80.60	78.30	73.90	72.71
5	5 (-1)	2 (-1)	75 (+1)	20 (-1)	65.40	66.50	58.20	57.60
6	9 (+1)	2 (-1)	75 (+1)	20 (-1)	79.30	80.10	70.50	70.63
7	5 (-1)	4 (+1)	75 (+1)	20 (-1)	78.20	78.10	75.40	74.00
8	9 (+1)	4 (+1)	75 (+1)	20 (-1)	87.50	89.20	81.80	84.04
9	5 (-1)	2 (-1)	45 (-1)	40 (+1)	65.20	61.70	61.40	56.34
10	9 (+1)	2 (-1)	45(-1)	40 (+1)	74.30	71.50	68.90	66.07
11	5 (-1)	4 (+1)	45 (-1)	40 (+1)	80.90	77.20	74.89	70.52
12	9 (+1)	4 (+1)	45(-1)	40 (+1)	87.20	84.30	79.50	77.27
13	5 (-1)	2 (-1)	75 (+1)	40 (+1)	73.80	73.20	69.30	66.25
14	9 (+1)	2 (-1)	75 (+1)	40 (+1)	84.70	84.20	74.20	75.72
15	5 (-1)	4 (+1)	75 (+1)	40 (+1)	84.80	83.90	77.40	76.25
16	9 (+1)	4 (+1)	75 (+1)	40 (+1)	89.60	92.30	82.20	82.74
17	3 (-2)	3 ($\pm$ 0)	60 ($\pm$ 0)	30 ($\pm$ 0)	56.20	61.20	43.20	52.04
18	11 (+2)	3 ($\pm$ 0)	60 ($\pm$ 0)	30 ($\pm$ 0)	82.30	82.00	73.60	71.82
19	7 ($\pm$ 0)	1 (-2)	60 ($\pm$ 0)	30 ($\pm$ 0)	60.50	64.10	55.40	60.03
20	7 ($\pm$ 0)	5 (+2)	60 ($\pm$ 0)	30 ($\pm$ 0)	87.60	88.60	85.20	87.62
21	7 ($\pm$ 0)	3 ($\pm$ 0)	30 (-2)	30 ($\pm$ 0)	53.70	62.80	48.01	57.72
22	7 ($\pm$ 0)	3 ($\pm$ 0)	90 (+2)	30 ($\pm$ 0)	89.70	85.20	81.60	78.96
23	7 ($\pm$ 0)	3 ($\pm$ 0)	60 ($\pm$ 0)	10 (-2)	72.00	72.90	59.40	61.68
24	7 ($\pm$ 0)	3 ($\pm$ 0)	60 ($\pm$ 0)	50 (+2)	82.10	85.80	70.10	74.88
25	7 ($\pm$ 0)	3 ($\pm$ 0)	60 ($\pm$ 0)	30 ($\pm$ 0)	78.20	80.00	63.07	64.83
26	7 ($\pm$ 0)	3 ($\pm$ 0)	60 ($\pm$ 0)	30 ($\pm$ 0)	80.80	80.00	65.80	64.83
27	7 ($\pm$ 0)	3 ($\pm$ 0)	60 ($\pm$ 0)	30 ($\pm$ 0)	81.0	80.0	65.63	64.83

3 Results and Discussion

Before determining the levels given in the matrix in Table 2, pre-studies were done, according to the studies conducted in the literature (Table 1), which are mostly for PS activation. Thermal and alkali activation of PS and PMS were studied for the points given in Table 4, and it was observed that the effect of pH and temperature were significant. Therefore, the level of pH was selected, starting from pH 3 to pH11 and the levels for temperature was ranged from 30 – 90°C. Since high degradation efficiencies were achieved under high PMS concentration and high required time, lower values of both parameters were chosen as levels (Table 2).

Table 4. Pre-studies for determining the levels of CCD

Runs	pH	PS Conc., mM	PMS Conc., mM	Time, min	Temperature, °C	Degradation Eff., %
1	7.0	5	-	60	70	89.5
2	7.0	5	-	60	90	95.0
3	2.5	5	-	60	70	80.6
4	2.5	5	-	60	30	75.6
5	7.0	-	5	60	70	62.1
6	11.0	-	5	60	70	99.3
7	2.5	-	5	60	70	88.1
8	2.5	-	5	60	30	88.1

According to the central composite design, the runs were designed in a batch mode as given in Table 3. The response of CCD was selected as OTC degradation. The PS and PMS processes were evaluated separately, and compared based on degradation, active species, and intermediate products.

3.1 Model Accuracy

All runs given in Table 3 were studied with the PS process by considering the concentrations of B parameter as PS concentrations (Table 2). Regarding the obtained responses (Table 3), the quadratic model was used as the most suitable model to explain the relationship between the experienced and the values of OTC degradation estimated using ANOVA results in the PS process. The results of the statistical analysis of ANOVA are shown in detail in Table 5. The results obtained in the studies with PS show that the oxidation performance gives satisfactory results. By considering the regression coefficients, the reliability between the actual data and the predicted

values of the responses was proved by the quadratic model. Variance analysis values were given in Table 5 to better understand the optimization performance of the study. The regression coefficient (R^2) was determined as above 90%, which shows the model performance is good. The fit of the model appears to be in good accordance with the R^2 with adjusted R^2 values. Besides, there is a slight difference between the experimental and predicted values shown in Table 3, resulting in a low coefficient of variation value (C.V. value). The accuracy and repeatability of the experiments were confirmed by this low C.V. value (C.V. <10%) (Can-Guven et al., 2020; Varank, 2020). The adequate precision value is required to be greater than 4 to measure the predicted response and the corresponding error value (the signal-to-noise ratio)(Rahdar et al., 2020). In this study, it was found to be over 4 (Table 5). The fitness of the model can be considered as desired. The non-significant lack of fit values can be submitted as the best fit (Varank, 2020).

Table 5. ANOVA results of the quadratic model for Heat-activated PS oxidation

Source	Sum of Squares	df	Mean Square	F-value	P-value	Significance
Model	2721.95	14	194.42	9.11	0.0002	
A-pH	653.93	1	653.93	30.65	0.0001	HS
B-PS/PMS	898.40	1	898.40	42.11	< 0.0001	HS
C-Temperature	751.44	1	751.44	35.22	< 0.0001	HS
D-Time	246.44	1	246.44	11.55	0.0053	S
AB	6.72	1	6.72	0.32	0.5850	NS
AC	1.31	1	1.31	0.06	0.8085	NS
AD	7.61	1	7.61	0.36	0.5615	NS
BC	22.09	1	22.09	1.04	0.3290	NS
BD	0.88	1	0.88	0.04	0.8426	NS
CD	8.70	1	8.70	0.41	0.5350	NS
A²	94.38	1	94.38	4.42	0.0572	NS
B²	17.67	1	17.67	0.83	0.3808	NS
C²	47.85	1	47.85	2.24	0.1601	NS
D²	0.52	1	0.52	0.03	0.8782	NS
Residual	256.02	12	21.34			
Lack of Fit	251.16	10	25.12	10.33	0.0914	NS
Pure Error	4.86	2	2.43			
Cor Total	2977.97	26				
R²	0.914					
Adjusted R²	0.814					
C.V. %	6.09					
Adeq. Precision	11.69					

HS: Highly significant, S: significant, NS: Non-significant

Besides, the P values of each parameter given in Table 5 were evaluated according to the 95% confidence interval. Parameters with a value of P less than 0.05 were considered as significant and those with a value lower than 0.0001 were considered as highly significant. It can be seen from Table 5 that the linear terms of the selected independent variables were significant, but quadratic forms were not so effective. The equation obtained based on these data is obtained as given in Eq.10.

$$y_1 = 80.02 + 5.225A + 6.117B + 5.60C + 3.208D - 0.65AB + 0.288AC - 0.688AD - 1.175BC - 0.225BD - 0.738CD - 2.104A^2 - 0.904B^2 - 1.492C^2 - 0.154D^2 \quad (\text{Eq.10})$$

The coefficients in Eq.10 assistance to understand the importance of the effect of variables on the response, in terms of both magnitude and signs. Therefore, the fact that all independent variables (A, B, C, and D) have positive coefficients indicates that these variables have a positive effect on OTC degradation. Rather, all the coefficients belong to the interaction, and the quadratic terms of the independent variables (except AC) have negative signs indicating that they have negative effects on OTC degradation. Moreover, the highest coefficient within all independent variables belongs to PS concentration. According to this information, time can be considered as the less effective parameter. Since the P-values of independent variables are significant, we can also express that all independent variables have a high impact on OTC degradation.

The same model used for the PS process was also modeled for the PMS process by applying the concentrations determined in the B parameter as PMS. The CCD is designed as quadratic and the predicted values of the model outputs were given in Table 2. The results obtained in the studies with PMS show that it gives acceptable results when the degradation performance is examined. The regression coefficient of the model was obtained as 0.89 and C.V was less than 10%. Besides, as mentioned above, the adequate precision value was used to measure the signal-to-noise ratio. A higher value than 4 shows the accuracy of the model. P-values of the parameters can also be seen in Table 6. The model was evaluated with a confidence interval of 95%, and it can be seen that the linear forms of the independent variables were the most effective within all components of the quadratic model. The equation obtained according to the ANOVA results was given in Eq.11.

$$y_2 = 64.833 + 4.944A + 6.898B + 5.31C + 3.301D - 0.745AB - 0.066AC - 0.89AD - 1.047BC - 1.60BD - 1.464CD - 0.726A^2 + 2.249B^2 + 0.876C^2 - 0.862D^2 \quad (\text{Eq.11})$$

Table 6. ANOVA results of the quadratic model for Heat-activated PMS oxidation

Source	Sum of Squares	df	Mean Square	F-value	P-value	Significance
Model	2951.37	14	210.81	6.90	0.0009	
A-pH	586.58	1	586.58	19.19	0.0009	HS
B-PS/PMS, mM	1141.95	1	1141.95	37.36	< 0.0001	HS
C-Temperature, °C	676.62	1	676.62	22.14	0.0005	HS
D-Time, min	261.54	1	261.54	8.56	0.0127	S
AB	8.93	1	8.93	0.2920	0.5988	NS
AC	0.07	1	0.07	0.0023	0.9629	NS
AD	12.64	1	12.64	0.4136	0.5322	NS
BC	17.53	1	17.53	0.5734	0.4635	NS
BD	40.87	1	40.87	1.34	0.2700	NS
CD	34.30	1	34.30	1.12	0.3103	NS
A²	11.22	1	11.22	0.3670	0.5559	NS
B²	107.95	1	107.95	3.53	0.0847	NS
C²	16.38	1	16.38	0.5359	0.4782	NS
D²	15.86	1	15.86	0.5190	0.4851	NS
Residual	366.80	12	30.57			
Lack of Fit	362.12	10	36.21	15.49	0.0621	NS
Pure Error	4.68	2	2.34			
Cor Total	3318.17	26				
R²	0.8895					
Adjusted R²	0.7605					
C.V. %	8.16					
Adeq. Precision	11.11					

HS: Highly significant, S: significant, NS: Non-significant

The Pareto chart also illustrates the influence of independent variables on OTC degradation using Eq. 12, where β_i represents the coefficient of the independent variables (Majumdar and Pal, 2020).

$$P_i = \left(\frac{\beta_i^2}{\sum \beta_i^2} \right) \cdot 100 (i \neq 0) \quad (\text{Eq.12})$$

Pareto chart was prepared for PS and PSM processes and showed in Figure 1a and Figure 1b, respectively. The independent parameters which are effective more than 1% are considered for

205 Pareto charts. For both processes, the most effective parameter can be revealed as PS/PMS
 206 concentration (B) and followed by temperature (C), pH (A), and time (D). The P values of the
 207 interaction and quadratic terms of the models were higher than 0.05 which shoes the low/non-
 208 impact on the OTC degradation. The percentage of the effects of these terms is less than 4%.

a.

b.

Figure 1. Pareto charts for (a) PS process and (b) PMS process

210 We can also analyze the adequacy of the model by the normal probability graphs which define the
211 difference between the predicted results and the experimental results. Normal probability plots
212 used to evaluate the normality of residues are obtained by plotting predicted residues versus
213 observed residues as given in Figure 2. It implies that the quadratic regression model that appears
214 to be distributed along a straight line is satisfactory.

215 Figure 2. Actual vs. predicted values for (a) PS and (b) PMS oxidation

3.2 Comparison of PS and PMS Processes

Three-dimensional (3D) response surface graphs show the effect of only two factors on OTC degradation efficiency, while the other two factors are fixed at the midpoint ($\alpha = 0$). Factors can be evaluated within the ranges given in Table 1. The effect of independent variables can be observed via the 3D plot generated via CCD. These plots were prepared for PS and PMS processes separately and the comparison of the processes was established accordingly. As can be seen from the surface graphs given in Figure 3, the OTC degradation efficiencies were increasing with the increment on all independent variables. This was also gathered from ANOVA results. The higher degradation efficiencies were expected with the increase of PS concentrations since it is the most important variable of the process (Figure 3.a)(Can-Guven et al., 2020). According to Figure 3.a, when the PS concentration was higher than 3mM, and pH is higher than pH7, the degradation efficiencies can be obtained at a higher value than 80%. As per Figure 3.b and Figure 3.c, with higher values than 60°C for temperature, 30 min, and pH7, the degradation efficiencies are higher than 80%. This can also be understood from the intercept of Eq.9, which is 80. All 3D figures were illustrated for OTC degradation efficiencies versus 2 independent variables, while the other two parameters were selected at the center point. The highest degradation efficiency can be seen in Figure 3.e as approximately 92% with the highest PS concentration (5 mM), highest time (50 min) at pH7 and 60°C.

Figure 3.b, Figure 3.d, and Figure 3.f show the effect of temperature with other independent variables on OTC degradation. Considering that the increase in temperature has a positive effect on both increasing the efficiency of sulfate radicals and degradation of OTC, a value at high temperature will be optimum as expected. Likewise, the effect of the pH factor is an effective parameter on PS processes. PS can be activated at low pH values but also at alkaline conditions. Therefore, the effect of pH was screened in a very broad spectrum (pH3 – pH 11). According to Figure 3.a, 3.b, and 3.c, OTC degradation obtained at alkaline conditions.

Figure 3. 3D plots for heat activated-PS oxidation

Figure 4. 3D plots for heat activated-PS oxidation

The linear effects of independent variables in Equation 10 are positive, which shows that all parameters are positively affecting. This can also be seen from Figure 4 that OTC degradation is linear to the increment in the values of each parameter. The highest coefficient within all independent variables belongs to PMS concentration, which shows that it is the most effective parameter within all. Similarly, it can be gathered from Figure 4 that the PMS concentration is the most effective parameter, while the effect of time is lower than the others. This effect of time, which is less than other parameters, can be seen from Figure 4.c, 4.e, and 4.f and also from P-Value from Table 5. The graph with the highest removal efficiency (approximately 98%) was attained in Figure 4.d, and it was obtained in the case where the PMS concentration was the highest. Also, from Figure 4.d, higher OTC degradation with the increment of temperature can be caused by the formation of hydroxyl radicals at higher temperatures. To have a higher degradation than 80%, all parameters should be in a higher alpha value than 0.9, which means that the conditions higher than pH9, 4 mM PMS concentration, 75°C, and 40 min of reaction time. However, this situation is different for the case where the PMS concentration is 5mM at the highest point, the effectiveness of all other parameters is low (Figure 4.a, 4.d, and 4.e). Especially, the time parameter is not affecting, when PMS concentration is 5mM; the OTC degradation efficiency is approximately 90% regardless of time (Figure 4.e). This shows that the effectiveness of PMS can be seen at the highest concentration.

3.3 Optimization of PS and PMS Processes

Eq. 10 and Eq. 11 were optimized to understand the conditions under which the highest removal efficiency is at the levels of the experimental matrix given in Table 2. Both processes were optimized taken into account all parameters, and it was obtained that the degradation efficiencies that could be obtained for PS and PMS processes were 89.7% and 84.0%, respectively (Table 7). Accordingly, the optimum pH is approximately 9, and the optimum temperature was obtained as 72.9 and 75.0°C for PS and PMS processes, respectively. It has been gathered that while 26.5 min of reaction time is needed for the PS process, 20 min is sufficient for PMS. Figure 2.e shows that the degradation efficiency is the same regardless of the time when the PS/PMS is 4mM. Nevertheless, a low reaction time is required, the efficiency of the PMS process was lower than the PS process. Ji et al. (2016) emphasized in their study that 240 min was needed to achieve 100% removal in the persulfate process they activated with heat (Table 1). Malakotian et al. (2019)

reported that for OTC removal, 90 min were needed for approximately 93% removal with 4mM PS they activated with magnetite and UV. In their sonocatalysis with peroxydisulfate study by Kumar Subramani et al. (2019), it was found that 1h was required for degradation of OTC at a concentration of 2mg/L with 99% yield (In this study, the temperature used is 55°C and the PS concentration was 1g/L). According to the literature and results of this study, it can be revealed that the use of PS is more effective than the PMS process.

Reaction pH is important in PS/PMS processes for two reasons, one is for conversion to sulfate radical and the other is that there are four different types of OTC at different pH. This may cause generated active species against different OTC types to give different reactions. Liu et al. (2016b) mentioned that the sulfate radical anion may have a negative effect on anionic and zwitterionic organic compounds. OTC molecule exists in the cationic form at acidic pHs, while it exists in zwitterionic form when pH is between pH3 and pH7. The reason for the low effects of both PS and PMS processes between pH 3-7 can also be explained in this way. To understand this issue, k_t values were calculated at the optimum point based on the data given in Table 7. PS and PMS concentration was selected as 4mM to obtain the same value, and the temperature was selected as 75°C. The calculation of k_t values was calculated based on Equation 13.

$$C = C_0 \cdot \exp(-k_t \cdot t) \quad (\text{Eq.13})$$

Where C_0 and C were the initial and effluent concentration (mg/L) at “t” time (min) and k_t is the pseudo-first-order constant (min^{-1}). Exponential function versus time was prepared at different pH values to calculate k_t , and the results can be seen in Figure 5. Accordingly, the optimum pH can also be obtained from k_t as pH 9. After pH 9, while the k_t values for PS were reduced, it stayed the same for the PMS process. The form of OTC^{2-} which exists on pH11 does not react well with PS activation (Liu et al., 2016b). Suggested that the active species on the PS process is known that mostly $\text{SO}_4\cdot^-$ radicals existed under alkaline conditions; the reaction of $\text{SO}_4\cdot^-$ radicals and OH^- can decrease the effectiveness of $\text{SO}_4\cdot^-$ radicals which causes low OTC degradation efficiencies (Eq.6). When k_t values at acidic and alkali conditions were compared, the PS process seems to be more effective. Since it is known that only $\text{SO}_4\cdot^-$ radicals exist at the PS process, it can be concluded that both $\text{SO}_4\cdot^-$ radicals are more effective than $\text{OH}\cdot$ radicals in both PS and PMS processes.

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Table 7. Optimum conditions for Heat activated-PS/PMS oxidation

Conditions	PS	PMS
A-pH	8.9	9.0
B-PS/PMS, mM	3.9	4.0
C-Temperature, °C	72.9	75.0
D-Time, min	26.5	20.0
Max. Removal efficiency, %	89.7	84.0

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Figure 5. k_t values at different pH values with Ps and PMS processes

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The accuracy of the model expresses with the confidence interval (Ulucan-Altuntas and Debik,

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2020) which is calculated via Equation 14.

$$CI = \bar{x} \pm z \frac{S}{\sqrt{n}} \quad (\text{Eq.14})$$

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Where CI is the confidence interval, $\bar{x}$ is the sample mean, z is the value of confidence level value,

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s is the sample standard deviation and n is the number of samples. The confidence level was

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selected as 95% for this study, thus, z was used as 1.96. CI was determined as ± 4.2 and ± 4.6 for

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PS and PMS processes. The studies were established three times at the optimum point given in

312 Table 7 for both processes and the results were 87.6 ± 4.2 and 80.2 ± 4.6 for PS and PMS processes,
313 respectively, which are acceptable for the prepared model.

314 Figure 6. UV-vis spectrum of OTC samples before and after treatment by (a) PS and (b) PMS
315 processes

To analyze the degradation intermediate products, UV-Visible wavelength spectrum was used for the samples studied at the optimum point given in Table 7. The spectrums of the samples before and after treatment by PS and PMS processes were given in Figure 6.a and Figure 6.b, respectively. Two wide peaks were observed at the initial OTC samples. While the wide peak between 320 nm and 400 nm disappeared in the effluent samples of both processes, the peak at 265 nm seen in the initial sample was shifted to 255 nm in the effluent sample of the PMS process (Fig.6.b) but was not observed in the PS process (Fig.6.a). Since OTC is a naphthol ring, naphthalene is an expected by-product as a result of degradation. The presence of naphthalene has been stated in the literature that the OTC compound will be formed by breaking the stable naphthol ring (Kumar Subramani et al., 2019). The wide peak seen at 255nm can be seen as the transformation of naphthene as a result of degradation. Looking at the absorbance values around 220 nm, an increase in height is seen as a result of both processes. This case shows simple acidic compounds with -C=O- bonds, such as acetic acid. This can be stated as the last step (by-product) of degradation. The issue of determining the degradation by-products and complete mineralization will be investigated in further studies.

Conclusion

This study was conducted to compare PS and PMS processes on OTC degradation by optimization with central composite design. The independent variables were selected as initial pH, PS/PMS concentration, temperature, and time for both processes in which PS/PMS concentration was determined as the most important variables within them. For both processes, the importance of the independent variables was determined as PS/PMS concentration > temperature > initial pH > time. According to CCD models, only the linear terms were concluded as the effective independent variables for both processes. Kinetic constants for pseudo-first-order for different pH values calculated at highest PS/PMS concentrations showed that PMS has slightly higher k constants, meaning better in OTC degradation. Kinetic constants were attained as 0.068 and 0.071 min⁻¹ for PS and PMS processes, respectively. According to optimum conditions, optimum pH is pH9, PS/PMS concentration is approximately 4 mM, the temperature is 72.9°C and 75°C and the required time was 26.5 min and 20 min for PS and PMS processes, respectively. Besides, according to the UV-vis spectrum, while the peak for OTC decreased for both processes, peak height at 225 nm showed that compounds with -C=O- bonds were increased at both PS and PMS processes All

results promote PS is more effective than the PMS process. In light of this information, additional processes can be used in PS/PMS activation to lower the required PS/PMS concentration.

Ethics declarations

- Completing Interest: The Authors declare that there is no conflict of interest.
- Ethical Approval: Not applicable (This study did not recruit any human/animal subjects.)
- Consent to Participate: Not applicable (This study did not recruit any human subjects.)
- Consent to Publish: Not applicable (This study is not published previously)

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Availability of data and materials

The datasets obtained during this study are available from the corresponding author on reasonable request.

Author contributions

All authors are contributed to designing the study. SYG, ECG, and FI are contributed to the whole experiments, KUA and GV helped partially on experiments. KUA, SYG, and GV were contributed to analyzing response surface methodology. KUA was the major contributor in writing the manuscript, while all authors were contributed to writing, revising, and finalizing the manuscript. All authors approved the final manuscript.

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452

Figures

a.

b.

Figure 1

Pareto charts for (a) PS process and (b) PMS process

a.

b.

Figure 2

Actual vs. predicted values for (a) PS and (b) PMS oxidation

Figure 3

3D plots for heat activated-PS oxidation

Figure 4

3D plots for heat activated-PS oxidation

Figure 5

kt values at different pH values with Ps and PMS processes

Figure 6

UV-vis spectrum of OTC samples before and after treatment by (a) PS and (b) PMS processes